050415   Polymer Properties Quiz 3

Polymer chains are well described on a local scale by the rotational isomeric state model and through computer simulations and calculations based on this model. For our purposes, this results in a base size of physical significance with an associated number of base units (Kuhn units). The polymer chain develops an overall shape and size through dynamic thermal equilibration with its environment. A fundamental tenet of modern polymer science is that the size (relative to the size of the Kuhn unit) and shape of such a polymer "coil" is independent of the details of the Kuhn unit. Coils can be classified as random (Brownian), self-avoiding (good solvent), or collapsed. Determination of the size and shape of dynamic polymer coils is a statistical problem since the "coil" is a disordered structure that fluctuates in time and space.

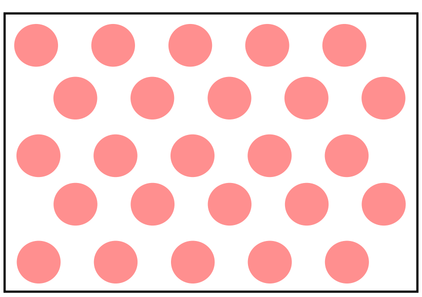
a) The coil size can be measured in a dynamic measurement through the hydrodynamic radius, R_H. Define R_H in terms of the friction factor, ξ, and solvent viscosity, η_0. Explain how the friction factor is generally related to the diffusion coefficient, D.

b) Give Fick's first and second laws. Design a hypothetical experiment using one of these laws to measure R_H from a polymer solution.

c) Static scattering measurements and computer simulations generally yield the radius of gyration, R_g, as a measure of the coil size. Give the two expressions for R_g described in class and show that the two expressions are identical.

d) For a rod with an aspect ratio (L/D) of 100 and a radius of 1 nm the measured hydrodynamic radius is about 1 nm. Calculate the radius of gyration for this rod by deriving an expression for R_g of a rod. Use your answer to judge the relative usefulness of R_g and R_H in describing chain aggregates that display large aspect ratios. (The derived expression should be $R_g^2 = \frac{R^2}{2} + \frac{(L/2)^2}{3}$. This can be obtained by integration over a differential volume element dV ~ rdrdl where the distance form R_G is given by $R^2 = (r^2 + l^2)$. You will need to integrate form r = 0 to R and from l = 0 to L/2 since R_G is at the center of the rod.)

e) The shape of a polymer coil is often described in scattering and in simulations by the pairwise correlation function g(r) or p(r). Using the rod throwing approach, sketch g(r) versus r for the following 2d structure and explain how g(r) was obtained. How does this correlation function differ from what you would expect for a disordered material such as a polymer coil?



050415 Quiz 3 Answers (1)

a) Stokes Law

$$\xi = 6\pi\eta_0 R_H$$

Fluctuation Dissipation Theorem

$$D = \frac{kT}{\xi}$$

b) $J = -D\frac{\partial c}{\partial x}$ $\quad J =$ flux

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

(i) Infinite Source

$\cdot x$

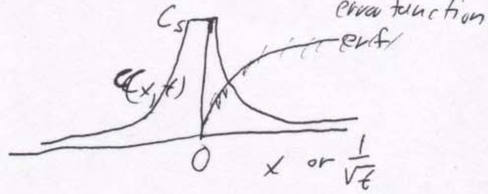
$C(x,0) = 0$

$C(0, \text{t all}) = C_s$

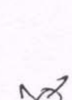
$C(\infty, t) = 0$

$$C(x,t) = C_s\left(1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right)$$

error function



(ii) Limited Source



$\cdot x$

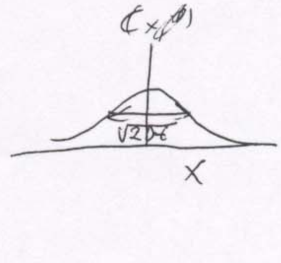
$C(x,0) = 0$

$\int C(x,t)\,dx = S$ constant amount of material

$C(x,\infty) = 0$

$$C(x,t) = \frac{S}{\sqrt{\pi D t}}\exp\left(\frac{-x^2}{4Dt}\right)$$

Notice This is a Gaussian in X with $\sigma = \sqrt{2Dt}$



For example Measure the polymer concentration using a refractometer at a distance x from a small pellet {limited source (long times)} if pellet is small; Infinite Source if pellet is large (short times)

②

Get D then use D to obtain ξ

$$\xi = \frac{kT}{D} = 6\pi\eta_0 R_H$$

$$\boxed{R_H = \frac{kT}{6\pi\eta_0 D}}$$

c)

$$(1) \quad R_g^2 = \frac{1}{N}\sum_{i=1}^{N} \langle (r_i - R_G)^2 \rangle$$

Average is over different chains + different configurations in time for one chain

$$(2) \quad R_g^2 = \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \langle (r_i - r_j)^2 \rangle$$

Here we consider one configuration of one chain for simplicity

$$(3) \quad R_G = \frac{1}{N}\sum_{i=1}^{N} r_i$$

Expand (2) using (3)

$$R_g^2 = \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \left((r_i - R_G) - (r_j - R_G)\right)^2$$

$$= \frac{1}{2N^2}\left\{N\left(\sum_{i=1}^{N} r_i - NR_G\right)^2 + N\left(\sum_{j=1}^{N} r_j - NR_G\right)^2 - 2N^2\sum_{i=1}^{N}(r_i - R_G)\sum_{j=1}^{N}(r_j - \right.$$

$\left(NR_G = \sum_{i=1}^{N} r_i \text{ from (3) so this term is } 0\right)$

$$= \frac{\cancel{2N}}{2N^{\cancel{2}}}\sum_{i=1}^{N}(r_i - R_G)^2 \equiv (1)$$

③

d)

$$R_g^2 = \frac{\int_0^R \int_0^{L/2} (r^2+l^2)\, r\,dr\,dl}{\int_0^R \int_0^{L/2} r\,dr\,dl}$$

$$= \frac{\int_0^R \left(\frac{Lr^3}{2} + \frac{L^3 r}{24} \right) dr}{\int_0^R \frac{Lr}{2}\, dr}$$

$$= \frac{\frac{LR^4}{8} + \frac{L^3 R^2}{48}}{\frac{LR^2}{4}}$$

$$= \frac{R^2}{2} + \frac{L^2}{12}$$

Here $R = 1$ nm

$L = 200$ nm.

$$R_g^2 = \frac{1}{2} + \frac{40{,}000}{12} \text{ nm}^2$$

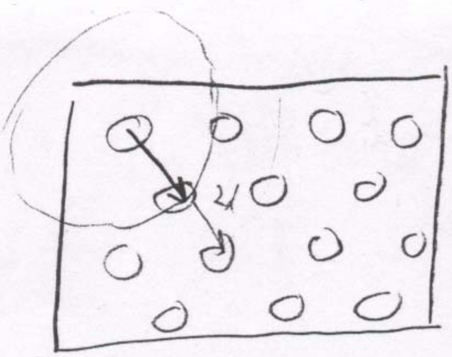
$$R_g = \sqrt{3{,}333.8} = 57.7 \text{ nm}$$

R_g is a better description of the size of the rod

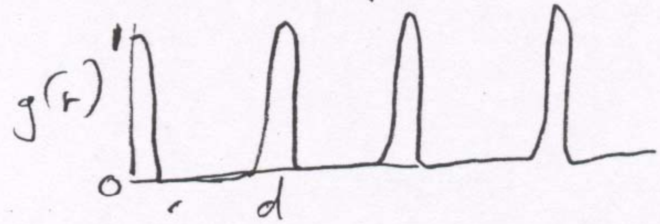
$L = 200$ nm $\quad R_g \cong 60$ nm

$R = 1$ nm $\quad R_H \sim 1$ nm

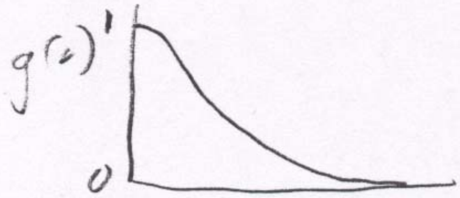
e



HCP Closest spacing



For a disorder Structure g(r) is a decay function



partly because $\rho(r) = \frac{N}{V} = N^{1-3/2} = N^{-1/2} \sim R^{-1}$

$R \sim N^{1/2} \sim N^{1/d_f}$

$V \sim N^{3/2} \sim N^{3/d_f}$

For a Gaussian Coil